Phase transitions and soft elasticity of smectic elastomers

Olaf Stenull and T. C. Lubensky
Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, PA 19104, USA
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Smectic-C elastomers can be prepared by crosslinking, e.g., liquid crystal polymers, in the smectic-A phase followed by a cooling through the smectic-A to smectic-C phase transition. This transition from $D_{\infty h}$ to C_{2h} symmetry spontaneously breaks rotational symmetry in the smectic plane as does the transition from a smectic-A to a biaxial smectic phase with D_{2h} symmetry. We study these transitions and the emergent elasticity of the smectic-C and biaxial phases in three related models and show that these phases exhibit soft elasticity analogous to that of nematic elastomers.

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Liquid crystalline elastomers [1] are remarkable materials that combine the orientational and positional order of liquid crystals [2] with the elastic properties of rubber. The traditional liquid crystalline nematic, cholesteric, smectic-A (SmA), smectic-C (SmC), and smectic-C^* phases all exist [1] in elastomeric forms. In this letter we investigate the properties of SmC and biaxial phases in elastomers formed via spontaneous symmetry breaking from SmA or uniaxial phases and, within mean-field theory, the phase transitions to them. We introduce and analyze phenomenological models for these transitions involving strains only and a model involving strains and the Frank director specifying the direction of local molecular order. Our primary result is that monodomain samples of the emerging biaxial and SmC phases (see Fig. 1), both of which break the continuous rotational symmetry in the smectic layers, exhibit soft elasticity characterized by the vanishing of certain elastic moduli and the associated absence of restoring forces to strains along specific symmetry directions. As in monodomain nematic elastomers [3, 4, 5] this soft elasticity is a consequence of the Goldstone theorem that requires any phase with a spontaneously broken continuous symmetry to have modes whose energy vanishes with wavenumber.

To keep our discussion as simple as possible, we will consider only smectic elastomers crosslinked in the SmA phase so that the smectic layers are locked to the crosslinked matrix [6]. Macroscopically, these SmA elastomers are simply uniaxial rubbers (or solids) with $D_{\infty h}$ symmetry, and we will treat them as such, though we will distinguish between the normal $\mathbf{N}$ to smectic layers and the direction of uniaxial anisotropy $\mathbf{e}$.

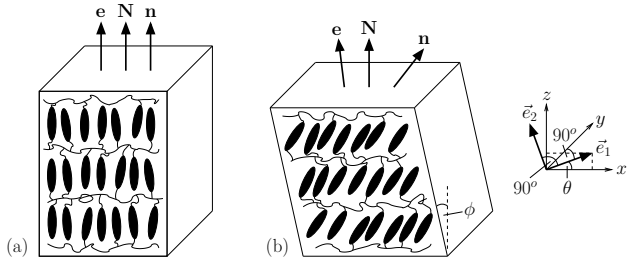

FIG. 1: Sample distortion and rotations of the Frank director $\mathbf{n}$, the uniaxial anisotropy axis $\mathbf{e}$, and the layer normal $\mathbf{N}$ in a transition from a (a) SmA to (b) a sheared SmC elastomer. In this geometry, the the smectic layers do not rotate. The figure corresponds to a shear strain $\gamma \approx u^0_{xz} < 0$ (see text).

We employ the usual Langrangian formalism [7] in which mass points in the undistorted medium, which we take as the reference space, are labelled by vectors $\mathbf{x}$. Mass points of the distorted medium are at positions $\mathbf{R}(\mathbf{x}) = \mathbf{x} + \mathbf{u}(\mathbf{x})$ in physical space, which we call the target space. Distortions of the reference medium are described by the Cauchy deformation tensor $\underline{\underline{\Lambda}}$ with components $\Lambda_{ij} = \partial R_i/\partial x_j \equiv \partial_j R_i$, $i, j = x, y, z$. Lagrangian elastic energies are expressed in terms of the nonlinear strain tensor $\underline{\underline{u}}$ with components $u_{ij}(\mathbf{x}) = \frac{1}{2}(\Lambda^T_{ik}\Lambda_{kj} - \delta_{ij}) = \frac{1}{2}(\partial_i u_j + \partial_j u_i + \partial_i u_k \partial_j u_k)$, which transforms as a tensor in the reference space and which is invariant with respect rotations in the target space. The elastic free energy density of a uniaxial elastomer to harmonic order in strains can be expressed as

$$f_{\rm uni} = \tfrac{1}{2}\, C_1\, u_{zz}^2 + C_2\, u_{zz} u_{ii} + \tfrac{1}{2}\, C_3\, u_{ii}^2 + C_4\, \hat{u}_{ab}^2 + C_5\, u_{az}^2, \qquad (1)$$

where we use the Einstein convention on repeated indices and where z is along the uniaxial axis and indices at the beginning of the alphabet $a, b, ..$ run over x and y only. The tensor $\hat{u}_{ab} = u_{ab} - \frac{1}{2}\delta_{ab} u_{cc}$ is the two-dimensional symmetric, traceless strain tensor. The elastic constant C_1 describes dilation or compression along z. C_4 and C_5 respectively describe shears in the plane perpendicular to the anisotropy axis and in the planes containing it. Relative volume change $\delta V/V = \det \underline{\underline{\Lambda}} - 1$ can be approximated by u_{ii} in our Landau expansion in powers of u_{ij}, and the incompressible limit relevant to most elastomers corresponds to $C_3 \to \infty$.

The harmonic free energy $f_{\rm uni}$ describes any uniaxial solid or elastomer, including SmA elastomers. However, to provide a complete description of SmA and SmC elastomers, we need to add terms that describe the smectic layers and the Frank director and their interactions with each other and with the elastic medium. Before adding

these terms, we will first investigate phase transitions in uniaxial elastomers in which either of the elastic constants C_4 or C_5 go to zero. The vanishing of C_4 and C_5 lead, respectively, to phases with D_{2h} (orthorhombic) and C_{2h} (triclinic) symmetry. We will then consider the smectic layers and director and show that the transition to the SmC phase, which has C_{2h} symmetry, is in fact identical to the one in which C_5 goes to zero.

Strain-only theory for $C_4 \to 0$: If C_4 or C_5 become negative, as they will in response to an instability toward biaxial or SmC ordering of constituent mesogens, terms higher order in strains must be added to Eq. (1) to ensure mechanical stability. If C_4 becomes negative, order of the shear strain $\hat{u}_{ab}$ sets in and higher order terms featuring $\hat{u}_{ab}$ have to be added which leads to the model elastic energy

$$f^{(1)}_{\rm uni} = f_{\rm uni} + A_1\, u_{zz}\hat{u}^2_{ab} + A_2\, u_{ii}\hat{u}^2_{ab} + B\,(\hat{u}^2_{ab})^2, \quad (2)$$

where we have dropped qualitatively inconsequential higher order terms. It will be useful in the analysis that follows to regroup the terms in $f^{(1)}_{\rm uni}$ by completing the squares in $\frac{1}{2}C_1u^2_{zz} + A_1u_{zz}\hat{u}^2_{ab}$, etc., and to reexpress it as a sum of two terms

$$f^{(1,1)}_{\rm uni} = \tfrac{1}{2}\,C_1 v^2_{zz} + C_2\, v_{zz}v_{ii} + \tfrac{1}{2}\,C_3\, v^2_{ii} + C_5\, u^2_{az} \quad (3)$$

$$f^{(1,2)}_{\rm uni} = C_4\,\hat{u}^2_{ab} + B_R\,(\hat{u}^2_{ab})^2, \quad (4)$$

where $v_{zz} = u_{zz} - \alpha\hat{u}^2_{ab}$, $v_{ii} = u_{ii} - \beta\hat{u}^2_{ab}$, and where β, which vanishes as $C_3 \to \infty$, B_R and α, which do not, are combinations of the coefficients in $f^{(1)}_{\rm uni}$. For a given $\hat{u}_{ab}$, $f^{(1)}_{\rm uni}$ is minimized when $u_{zz} = \alpha\hat{u}^2_{ab}$ and $u_{ii} = \beta\hat{u}^2_{ab}$. The equilibrium value of $\hat{u}_{ab}$, $\hat{u}^0_{ab} = S(c_ac_b - \frac{1}{2}\delta_{ab})$, where $\mathbf{c}$ is a unit vector in the xy plane, is determined by minimizing $f^{(1,2)}_{\rm uni}$. The result is $S = 0$ for $C_4 > 0$, and $S = \pm\sqrt{-C_4/B_R}$ for $C_4 < 0$. The equilibrium strain $\underline{\underline{u}}^0 = \frac{1}{2}(\underline{\underline{\Lambda}}^{0T}\underline{\underline{\Lambda}}^0 - \underline{\underline{\delta}})$ is diagonal with components $u^0_{xx} = \frac{1}{2}S + \frac{1}{4}(\beta-\alpha)S^2$, $u^0_{yy} = -\frac{1}{2}S + \frac{1}{4}(\beta-\alpha)S^2$, and $u^0_{zz} = \frac{1}{2}\alpha S^2$. The new state is biaxial with D_{2h} symmetry.

To determine the elastic properties of the new state, we expand $f^{(1)}_{\rm uni}$ in powers of $\delta\underline{\underline{u}} = \underline{\underline{u}} - \underline{\underline{u}}^0$. Since the equilibrium values of v_{zz}, v_{ii} and u_{az} are zero, the expansion of $f^{(1,1)}_{\rm uni}$ is trivial. The structure of $f^{(1,2)}_{\rm uni}$ is identical to that of an xy model, and it has no restoring force in the ordered phase for δu_{xy}: $\delta f^{(1,2)}_{\rm uni} = B_RS^2(\delta u_{xx} - \delta u_{yy})^2$. Thus it is clear that $\delta f^{(1)}_{\rm uni}$ does not depend on δu_{xy} to harmonic order, i.e., the system is soft with respect to shears in the xy plane of the original reference material.

The strain $\delta\underline{\underline{u}}$ describes distortions relative to the new biaxial reference state measured in the coordinates of the original uniaxial state. It is customary, however, to express the elastic energy in terms of a strain $\underline{\underline{u}}' = (\underline{\underline{\Lambda}}^{0T})^{-1}\delta\underline{\underline{u}}\,(\underline{\underline{\Lambda}}^0)^{-1}$ measured in the coordinates $x'_i = x_i + u^0_i = \Lambda^0_{ij}x_j$ of the new state. $\underline{\underline{\Lambda}}^0$ is not uniquely determined by $\underline{\underline{u}}^0$; rotations in the target space change $\underline{\underline{\Lambda}}^0$ but do not change $\underline{\underline{u}}^0$. In the present case, it is natural to choose $\underline{\underline{\Lambda}}^0$ to be diagonal, i.e., not to rotate the strain strain after the transition. The elastic energy of the biaxial state to harmonic order in the new strains is then

$$\begin{aligned} f^{\rm soft}_{D_{2h}} = {} & \tfrac{1}{2}\,C_{zzzz}\,(u'_{zz})^2 + C_{xzxz}\,(u'_{xz})^2 + C_{yzyz}\,(u'_{yz})^2 \\ & + C_{zzxx}\,u'_{zz}u'_{xx} + C_{zzyy}\,u'_{zz}u'_{yy} + \tfrac{1}{2}\,C_{xxxx}\,(u'_{xx})^2 \\ & + \tfrac{1}{2}\,C_{yyyy}\,(u'_{yy})^2 + C_{xxyy}\,u'_{xx}u'_{yy}, \end{aligned} \quad (5)$$

where the elastic constants depend on the original elastic constants featured in Eq. (2) and the order parameter S, and for $S \to 0$ this energy reduces to the uniaxial energy (1). If we take the incompressible limit, $C_3 \to \infty$, the specifics of the new elastic constants are affected but the form of the elastic energy (5) remains the same.

Because there was no δu_{xy} term in the expansion of $f^{(1)}_{\rm uni}$, there is no term proportional to u'^2_{xy} as there would be in conventional orthorhombic systems. Thus, there is no restoring force to xy-stresses, i.e., to opposing forces along $\pm x$ applied to opposite surfaces perpendicular to y or opposing forces along $\pm y$ applied to opposite surfaces perpendicular to x. In addition, as is the case for stresses perpendicular to the anisotropy axis in a nematic elastomer [4, 5], it requires no stress to stretch the sample along y direction, up to a critical strain value. The same soft mode and many more were predicted by Warner and Kutter [8] for biaxial nematics forming spontaneously from an isotropic elastomer.

Strain-only theory for $C_5 \to 0$: When C_5 is driven negative the uniaxial state becomes unstable to shear in the planes containing the anisotropy axis, and the uniaxial energy (1) must be augmented with higher order terms involving u_{az} to stabilize the system,

$$\begin{aligned} f^{(2)}_{\rm uni} = {} & f_{\rm uni} + D_1\, u_{zz}u^2_{az} + D_2\, u_{ii}u^2_{az} + D_3\,\hat{u}_{ab}u_{az}u_{bz} \\ & + E\,(u^2_{az})^2, \end{aligned} \quad (6)$$

where we omitted all unimportant symmetry-compatible higher order terms. To study the ordered phase of this free energy when $C_5 < 0$, we proceed in much the same way as we did for the biaxial state of $f^{(1)}_{\rm uni}$. We complete squares to write $f^{(2)}_{\rm uni}$ as the sum of two terms:

$$f^{(2,1)}_{\rm uni} = \tfrac{1}{2}\,C_1\, w^2_{zz} + C_2\, w_{ii}w_{zz} + \tfrac{1}{2}\,C_3\, w^2_{ii} + C_4\, w^2_{ab} \quad (7)$$

$$f^{(2,2)}_{\rm uni} = C_5\, u^2_{az} + E_R\,(u^2_{az})^2, \quad (8)$$

where $w_{zz} = u_{zz} - \sigma u^2_{az}$, $w_{ii} = u_{ii} - \tau u^2_{az}$, and $w_{ab} = \hat{u}_{ab} - \omega(u_{az}u_{bz} - \frac{1}{2}\delta_{ab}u^2_{cz})$ where σ, τ ($\to 0$ as $C_3 \to \infty$), ω, and E_R are functions of the parameters in $f^{(2)}_{\rm uni}$. The equilibrium value of u_{az} is determined by minimizing $f^{(2,2)}_{\rm uni}$, which has xy symmetry. For $C_5 > 0$, $u_{az} = 0$; for $C_5 < 0$ and order along x, $u^0_{xz} \equiv S = \pm\sqrt{-C_5/(2E_R)}$, and $u^0_{yz} = 0$. The other components of $\underline{\underline{u}}^0$ are $u^0_{zz} = \sigma S^2$,

$u^0_{xx} = \frac{1}{2}(\tau+\omega-\sigma)S^2$, and $u^0_{yy} = \frac{1}{2}(\tau-\omega-\sigma)S^2$. Unlike the biaxial case, $\underline{\underline{u}}^0$ is not diagonal; it has nonvanishing xz and zx components that lead to C_{2h} rather than D_{2h} symmetry. Expanding $f^{(2)}_{\rm uni}$ in powers of $\delta\underline{\underline{u}} = \underline{\underline{u}} - \underline{\underline{u}}^0$, we find that $\delta f^{(2,2)}_{\rm uni} = 4E_R S^2(\delta u_{xz})^2$ is independent of δu_{yz}, and we might naively expect the system to exhibit softness with respect to u_{yz}. This, however, is not the case because $f^{(2,1)}_{\rm uni}$ depends on δu_{yz} via the C_4 term: $2C_4(\delta u_{xy} - \omega S\,\delta u_{zy})^2$. Thus, the softness of the ordered phase with C_{2h} symmetry is more subtle than that of the biaxial phase with D_{2h} symmetry.

To determine the energy of strains relative to the new ground state, we need to choose how we define our new coordinate system relative to it. It is easiest to visualize the new state as emerging from a simple shear as shown in Fig. 1 in which $\Lambda^0_{xz} = \partial R^0_x/\partial z \equiv \gamma$ is nonzero but $\Lambda^0_{zx} = \partial R^0_z/\partial x = 0$. In this case, the only nonzero components of $\underline{\underline{\Lambda}}^0$ are the diagonal components and Λ^0_{xz} which can be expressed in terms of $\underline{\underline{u}}^0$: $\Lambda^0_{xx} = \sqrt{1+2u^0_{xx}}$, $\Lambda^0_{yy} = \sqrt{1+2u^0_{yy}}$, $\Lambda^0_{xz} = \gamma = 2u^0_{xz}/\Lambda^0_{xx}$, and $\Lambda^0_{zz} = \sqrt{1+2u^0_{zz}-\gamma^2}$. The elastic energy can now be written in terms of $\underline{\underline{u}}' = (\underline{\underline{\Lambda}}^{0T})^{-1}\delta\underline{\underline{u}}\,(\underline{\underline{\Lambda}}^0)^{-1}$ as

$$
\begin{aligned}
f^{\rm soft}_{C_{2h}} &= \tfrac{1}{2}\,\bar{C}\left[\cos\theta\,u'_{xy} + \sin\theta\,u'_{yz}\right]^2 + \tfrac{1}{2}\,C_{zzzz}\,(u'_{zz})^2 \\
&+ C_{xzxz}\,(u'_{xz})^2 + C_{zzxx}\,u'_{zz}u'_{xx} + C_{zzyy}\,u'_{zz}u'_{yy} \\
&+ \tfrac{1}{2}\,C_{xxxx}\,(u'_{xx})^2 + \tfrac{1}{2}\,C_{yyyy}\,(u'_{yy})^2 + C_{xxyy}\,u'_{xx}u'_{yy} \\
&+ C_{xxxz}\,u'_{xx}u'_{xz} + C_{yyxz}\,u'_{yy}u'_{xz} + C_{zzzz}\,u'_{zz}u'_{xz}, \qquad (9)
\end{aligned}
$$

where the angle θ and the elastic constants $\bar{C}$, C_{zzzz} and so on depend on the original elastic constants in Eq. (6) and S so that one retrieves the uniaxial energy (1) for $S \to 0$. To lowest order in S, $\tan\theta = \omega S$. The elastic energy (9) has only 12 (including θ) rather than the 13 elastic constants of conventional triclinic solids [9]. There are only two rather than three independent elastic constants in the subspace spanned by u'_{xy} and u'_{yz}. With the introduction of $\vec{v} = (u'_{xy}, u'_{zy})$, elastic energies in this subspace can be expressed as $\frac{1}{2}\vec{v}\cdot\overleftrightarrow{m}\cdot\vec{v}$ where $\overleftrightarrow{m}$ is a 2×2 matrix. In general $\overleftrightarrow{m}$ has two independent eigenvalues m_1 and m_2 with respective associated orthnormal eigenvectors $\vec{e}_1$ and $\vec{e}_2$ with respect to which $\overleftrightarrow{m}$ is diagonal: $\vec{v}\cdot\overleftrightarrow{m}\cdot\vec{v} = m_1(\vec{e}_1\cdot\vec{v})^2 + m_2(\vec{e}_2\cdot\vec{v})^2$. The first terms in Eq. (9) is of the form $\frac{1}{2}m_1(\vec{e}_1\cdot\vec{v})^2$ with $m_1 = \overline{C}$ and $\vec{e}_1 = (\cos\theta, \sin\theta)$, and we conclude that $m_2 = 0$. Thus distortions along $\vec{e}_2 = (-\sin\theta, \cos\theta)$, i.e., distortions for which $\vec{v} \parallel \vec{e}_2$ cost no energy (see Fig. 1). Stated differently, there are no restoring forces to stress $-\sin\theta\,\sigma_{xy} + \cos\theta\,\sigma_{zy} = e_{2i}\,\sigma_{iy}$, i.e., to stress in the xz plane directed along $\vec{e}_2$ or stress in the plane perpendicular to $\vec{e}_2$ directed along y.

Theory with director and smectic layers: The following theory generalizes the achiral limit of a continuum theory for SmC^* elastomers by Terentjev and Warner [10] in a formalism that ensures invariance with respect to arbitrary rather than infinitesimal rotations of both the director and mass points.

In traditional uncrosslinked liquid crystals, there is no reference space, and all physical fields like the smectic layer-displacement field U, the layer normal $\mathbf{N}$, and the Frank director $\mathbf{n}$ are defined at real or target space points $\mathbf{R}$ and they transform as scalars, vectors, and tensors under rotations in the target space. In the Lagrangian theory of elasticity, fields are defined at reference space points $\mathbf{x}$, and they transform into themselves under the symmetry operations of that space. To develop a theory of liquid-crystalline elastomers, it is necessary to combine target-space liquid crystalline fields and reference space elastic variables to produce scalars that are invariant under arbitrary rotations in the target space and under symmetry operations of the reference space. This requires that we be able to represent vectors and tensors in either space [5]. The matrix polar decomposition theorem [11] applied to the Cauchy tensor $\underline{\underline{\Lambda}}$ provides a route to this representation. Like any non-singular matrix, $\underline{\underline{\Lambda}}$ can be decomposed into the product of an orthogonal matrix $\underline{\underline{O}}$ times a symmetric matrix: $\underline{\underline{\Lambda}} = \underline{\underline{O}}\,\underline{\underline{M}}^{1/2}$, where $\underline{\underline{M}}^{1/2}$ is the symmetric square root of the symmetric matrix $\underline{\underline{M}} = (\underline{\underline{\Lambda}}^T\underline{\underline{\Lambda}}) = (\underline{\underline{1}} + 2\underline{\underline{u}})$, which depends only on the symmetric strain $\underline{\underline{u}}$, and $\underline{\underline{O}} = \underline{\underline{\Lambda}}\,\underline{\underline{M}}^{-1/2}$. The orthogonal matrix $\underline{\underline{O}}$ converts (or rotates) any reference space vector $\tilde{\mathbf{a}}$ to a target space vector $\mathbf{a}$ via $\mathbf{a} = \underline{\underline{O}}\cdot\tilde{\mathbf{a}}$ and a target-space vector to a reference space vector via $\tilde{\mathbf{a}} = \underline{\underline{O}}^T\cdot\mathbf{a}$. Equipped with $\underline{\underline{O}}$, we can rotate the target space director $\mathbf{n}$ to a reference space vector $\tilde{\mathbf{n}} \equiv (\tilde{\mathbf{c}}, \tilde{n}_z)$, where $\tilde{n}_z = \sqrt{1-\tilde{c}_a^2}$, and rotate the reference space anisotropy vector $\tilde{\mathbf{e}} = (0,0,1)$ to a target-space vector $\mathbf{e} = \underline{\underline{O}}\cdot\tilde{\mathbf{e}}$. From these, we can form invariant couplings like $(\tilde{\mathbf{n}}\cdot\tilde{\mathbf{e}})^2 = (\mathbf{n}\cdot\mathbf{e})^2 = 1-\tilde{c}_a^2$, $\tilde{c}_a u_{ab}\tilde{c}_b$, and $\tilde{c}_a u_{az}\tilde{n}_z$ as building blocks the elastic energy.

To treat smectic layers, we need to discuss in more detail the smectic displacement field U and the layer normal $\mathbf{N}$. The smectic mass-density-wave amplitude for a system with layer spacing d has a phase $\phi(\mathbf{R}) = q_0[R_z - U(\mathbf{R})]$ where $q_0 = 2\pi/d$. Since there is a one-to-one mapping from the reference space points $\mathbf{x}$ to the target-space points $\mathbf{R}(\mathbf{x})$, we can express ϕ as a function of $\mathbf{x}$ as $\phi(\mathbf{x}) = q_0[z + u_z(\mathbf{x}) - U(\mathbf{R}(\mathbf{x}))]$. We are only considering systems crosslinked in the smectic phase. In these systems, the smectic mass-density wave cannot translate freely relative to the reference material, and there is a term in the free-energy density $\frac{1}{2}A(u_z - U)^2$ that locks the smectic field U to the displacement field u_z [6]. In what follows, we will take this lock-in as given and set $U = u_z$. The layer normal in the target space is $N_i = \nabla_i\phi/|\boldsymbol{\nabla}\phi|$, where $\nabla_i\phi \equiv \partial\phi/\partial R_i = \partial_j\phi\Lambda^{-1}_{ji}$. Thus, when U is locked to u_z, $N_i = [(\underline{\underline{M}}^{-1})_{zz}]^{-1/2}\Lambda^{-1}_{zi}$, $\tilde{N}_i = [(\underline{\underline{M}}^{-1})_{zz}]^{-1/2}M^{-1/2}_{zi}$, and to harmonic order in $\tilde{c}_a$

and u_{ij}, $\tilde{\mathbf{N}}\cdot\tilde{\mathbf{n}} = \mathbf{N}\cdot\mathbf{n} = 1 - \tilde{c}_a^2 - u_{za}\tilde{c}_a + \cdots$.

We can now develop a full phenomenological free energy for the SmA–to–SmC transition in an elastomer. In the equilibrium SmA phase, the director is parallel to both the layer normal $\mathbf{N}$ and the anisotropy axis $\mathbf{e}$, which are parallel to each other, and there are energy costs proportional to $(\tilde{\mathbf{N}}\cdot\tilde{\mathbf{n}})^2$ and $(\tilde{\mathbf{e}}\cdot\tilde{\mathbf{n}})^2$ associated with deviations from this equilibrium. These combine to yield a term in the free-energy density proportional to $\tilde{c}_a^2$ and higher order terms involving the strain and strain-director coupling. With the addition of higher order terms in $(\tilde{\mathbf{N}}\cdot\tilde{\mathbf{n}})^2$ and $(\tilde{\mathbf{e}}\cdot\tilde{\mathbf{n}})^2$ to stabilize the SmC phase, the free energy up to inconsequential higher order terms becomes

$$f = f_{\rm uni} + f_{\rm tilt} + f_{\rm coupl}, \tag{10}$$

where $f_{\rm uni}$ is the uniaxial energy (1) and

$$f_{\rm tilt} = \tfrac{1}{2}\, r\, \tilde{c}_a^2 + \tfrac{1}{4}\, g\, (\tilde{c}_a^2)^2, \tag{11}$$

$$f_{\rm coupl} = \lambda_1\, \tilde{c}_a^2 u_{zz} + \lambda_2\, \tilde{c}_a^2 u_{bb} + \lambda_3\, \tilde{c}_a \hat{u}_{ab} \tilde{c}_b + \lambda_4\, \tilde{c}_a u_{az} \tilde{n}_z. \tag{12}$$

When $\lambda_1 = \lambda_2 = \lambda_3 = 0$, this model is equivalent to that studied in Ref. [10] when polarization is ignored.

We can now analyze the transition to the SmC phase in exactly the same way as we did in the strain only model. We complete the squares involving the strains and the director-strain couplings. The result is an expression for the free energy that is the sum of a term $f^{(1)}$ quadratic in shifted strains of the form $u_{zz} + \rho\tilde{c}_a^2$, etc. and a term $f^{(2)} = \frac{1}{2}\, r_R\, \tilde{c}_a^2 + \frac{1}{2}\, g_R\, (\tilde{c}_a^2)^2$ depending only on $\tilde{c}_a$, where $r_R = r - \lambda_4^2/(2C_5)$. With $\tilde{\mathbf{c}}$ chosen to align along x, minimization yields $\tilde{c}_x^0 \equiv S = \pm\sqrt{-r_R/g_R}$, $u_{xz}^0 = -\lambda_4 S/(2C_5)$ and diagonal components of $\underline{\underline{u}}^0$ proportional to S^2. As anticipated from the strain-only model for $C_5 \to 0$, the SmC phase is a sheared biaxial phase with C_{2h} symmetry. If $\tilde{c}_a$ is integrated out of f, the result is identical to $f_{\rm uni}$ with C_5 renormalized to $C_{5,R} = C_5 - \lambda_4^2/(2r)$, which vanishes at $r_R = 0$.

To address the elastic properties of the SmC phase within our last model, we expand the complete elastic energy (10) in terms of $\delta\underline{\underline{u}} = \underline{\underline{u}} - \underline{\underline{u}}^0$ and $\delta\tilde{\mathbf{c}} = \tilde{\mathbf{c}} - \tilde{\mathbf{c}}^0$. Since $f^{(2)}$ has xy symmetry, its expansion has a $(\delta\tilde{c}_x)^2$ but no $(\delta\tilde{c}_y)^2$ term. The expansion of $f^{(1)}$ has terms quadratic in $\delta\underline{\underline{u}}$ and couplings between $\delta\underline{\underline{u}}$ and $\delta\tilde{c}_a$. Since $\delta\tilde{c}_x$ is massive, it can be integrated out. Converting the resulting expression to the strain variable $\underline{\underline{u}}'$ of the SmC state, we obtain an elastic energy that is identical in form to Eq. (9) but with an additional term proportional to $[\delta\tilde{c}_y + \mu(u'_{xy} + \zeta u'_{yz})]^2$, where μ and ζ are dimensionless coefficients that depend on the original elastic constants and S. This expression shows clearly that $\delta\tilde{c}_y$ can relax locally to $-\mu\left(u'_{xy} + \zeta u'_{yz}\right)$ to eliminate the dependence of the elastic energy on $u'_{xy} + \zeta u'_{yx}$ and produce an energy with softness identical to that of Eq. (9).

The above analysis provides us with the strain $\underline{\underline{u}}^0$ and the c-director $\tilde{\mathbf{c}}^0$ in the coordinates of the reference space without rotation. To visualize what happens to $\mathbf{e}$, $\mathbf{N}$, and $\mathbf{n}$ in the SmC phase, it is useful to consider the simple shear of Fig. 1 in which $\tan\phi = \Lambda_{xz}^0 = \gamma$, and $\Lambda_{zx}^0 = 0$. To lowest order in S, $\gamma = 2u_{xz}^0 = -\lambda_4 S/C_5$, and $O_{ij} = \delta_{ij} + \frac{1}{2}\epsilon_{izj}\gamma$. Then $\mathbf{n} \approx (n_x, 0, 1)$ where $n_x = S + \frac{1}{2}\gamma$, and $e_i = O_{iz} = (\frac{1}{2}\gamma, 0, 1)$. Thus, at the transition $\mathbf{e}$ and $\mathbf{n}$ rotate relative to $\mathbf{N}$ by different amounts. The layer normal vector $\mathbf{N}$, however, remains fixed in the chosen geometry: $N_i \sim \Lambda_{zi}^{-1}$ only has a non-vanishing z component and is equal to $(0, 0, 1)$. Thus, the smectic layers remain parallel to the x-axis as one would intuitively expect in the chosen geometry.

Concluding remarks: We have presented models for transitions from uniaxial SmA elastomers to biaxial and SmC elastomers, and we have calculated the nature of the soft elasticity, required by symmetry, of monodomain samples of these phases. We hope that our work encourages experiments to probe this soft elasticity.

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